

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

This is a U.S. Patent Application for:

Title: **FORMING FERROELECTRIC Pb(Zr,Ti)O<sub>3</sub> FILMS**

Inventor #1: STEPHEN R. GILBERT  
Address: 116 Frederick Street #33, San Francisco, CA 94117  
Citizenship: United States

Inventor #2: KAUSHAL SINGH  
Address: 2118 San Rafael Avenue, Santa Clara, CA 95054  
Citizenship: India

Inventor #3: SANJEEV AGGARWAL  
Address: 8421 High Meadows Dr., Plano, TX 75025  
Citizenship: India

Inventor #4: STEVAN HUNTER  
Address: 1900 Unity Ct., Fort Collins, CO 80528  
Citizenship: United States

**EXPRESS MAIL CERTIFICATE OF MAILING**

EXPRESS MAIL NO.: E ~~K176606142~~ US

DATE OF DEPOSIT: Aug 8, 2001

I hereby certify that I am causing this paper or fee to be deposited with the United States Postal Service "Express Mail Post Office to Addressee" service on the date indicated above and that this paper or fee has been addressed to the Assistant Commissioner for Patents, Washington, D.C. 20231.

Katherine Lopez Diangson

(Typed or printed name of person mailing paper or fee)

Katherine Lopez Diangson

(Signature of person mailing paper or fee)

August 8, 2001

(Date signed)

# FORMING FERROELECTRIC $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ FILMS

## TECHNICAL FIELD

This invention relates to systems and methods of forming ferroelectric  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT) films, including ferroelectric PZT films for use in ferroelectric random access memory devices.

## BACKGROUND

Today, several trends exist in the semiconductor device fabrication industry and the electronics industry that are driving the development of new material technologies. First, devices are continuously getting smaller and smaller and requiring less and less power. A reason for this is that more personal devices are being fabricated which are very small and portable, thereby relying on a small battery as its supply source. For example, cellular- phones, personal computing devices, and personal sound systems are devices that are in great demand in the consumer market. Second, in addition to being smaller and more portable, personal devices are requiring more computational power and on-chip memory. In light of these trends, there is a need in the industry to provide a computational device that has a fair amount of memory and logic functions integrated onto the same semiconductor chip. Preferably, this computation device will include a non-volatile memory so that if the battery dies, the contents of the memory will be retained. Examples of conventional non-volatile memories include electrically erasable, programmable read only memories and flash EEPROMs.

A ferroelectric memory (FeRAM) is a non-volatile memory that utilizes a ferroelectric material as a capacitor dielectric situated between a bottom electrode and a top electrode. Ferroelectric materials, such as  $\text{SrBi}_2\text{Ta}_2\text{O}_9$  (SBT) and  $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$  (PZT), are being used in the fabrication of a wide variety of memory elements, including ferroelectric random access memory (FeRAM) devices. In general, ferroelectric memory elements are non-volatile because of the bistable polarization state of the material. In addition, ferroelectric memory elements may be programmed with relatively low voltages (e.g., less than 5 volts) and are characterized by relatively fast access times (e.g., less than 40 nanoseconds) and operational robustness over a large number of read and write cycles. These

memory elements also consume relatively low power, may be densely packed, and exhibit radiation hardness.

Recent efforts to develop fabrication processes for ferroelectric materials have focused on integrating FeRAM technology with semiconductor integrated circuit technology. Accordingly, such efforts have focused on scaling FeRAM capacitor areas, cell sizes and operating voltages downward in accordance with the scale of current integrated circuit dimensions. In addition to small lateral dimensions (i.e., dimensions parallel to the film surface), the ferroelectric dielectric must be relatively thin and must have a relatively low coercive field to achieve FeRAM devices having low operating voltages.

Recently, PZT has been demonstrated to be scalable to relatively small lateral dimensions and low operating voltages. For example, International Patent Publication No. WO 00/49646 discloses a process for forming a scalable PZT material by liquid delivery metalorganic chemical vapor deposition (MOCVD) without PZT film modification techniques, such as acceptor doping or use of film modifiers (e.g., Nb, Ta, La, Sr, Ca, and the like). In accordance with this process, liquid precursor solutions of the component metals are mixed and flash vaporized. The resulting source reagent vapor is introduced into a chemical vapor deposition chamber where the PZT film is deposited on a substrate. In one embodiment, the metalorganic precursors are lead bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (hereinafter "Pb(thd)<sub>2</sub>") as a Pb precursor, titanium bis(isopropoxide)bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (hereinafter "Ti(O-i-Pr)<sub>2</sub>(thd)<sub>2</sub>") as a Ti precursor, and zirconium tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionate) (hereinafter "Zr(thd)<sub>4</sub>") as a Zr precursor. In another embodiment, the lead precursor is lead bis(2,2,6,6-tetramethyl-3,5-heptanedionate) N, N', N"-pentamethyl diethylenetriamine (hereinafter "Pb(thd)<sub>2</sub>pmdeta") and the zirconium precursor is zirconium bis(isopropoxide)bis(2,2,6,6-tetramethyl-3,5-heptanedionate) (hereinafter "Zr(O-i-Pr)<sub>2</sub>(thd)<sub>2</sub>"). The solvent media used in the liquid delivery MOCVD process is selected to be compatible with the specific metalorganic precursors used for forming the PZT thin film materials and efficacious in the constituent liquid delivery and CVD process steps. Illustrative multi-component solvent compositions include: tetrahydrofuran: isopropanol: tetraglyme in a 8:2:1 volume ratio; octane: decane: polyamine in a 5:4:1 volume

ratio; and octane: polyamine in a 9:1 volume ratio. According to the WO  
00/49646 patent publication, the resulting PZT material is pulse length scalable or  
E-field scalable, or both, and is useful for ferroelectric capacitors having dielectric  
thicknesses that range from about 20 nanometers to about 150 nanometers and  
5 having lateral dimensions that extend down to as small as 0.15 micrometers.

Chemical vapor deposition (CVD) is a particularly attractive method for  
forming thin PZT films because CVD is readily scaled up to production runs and  
because CVD technology is sufficiently mature and developed that CVD may be  
applied readily to new film processes. In general, CVD requires that the element  
10 source reagents (i.e., the precursor compounds and complexes containing the  
elements or components of interest) must be sufficiently volatile to permit gas  
phase transport into the chemical vapor deposition reactor. The elemental  
component source reagents should decompose in the CVD reactor for deposition  
on the desired substrate surface at the desired growth temperatures. Premature  
15 gas phase reactions leading to particulate formation should be avoided. In  
addition, the source reagents should not decompose in the transport lines before  
reaching the reactor deposition chamber. In sum, in order to deposit CVD films  
having desirable properties, the stoichiometry and other process conditions must  
be controlled for a given baseline chemistry to create a transport window that  
20 enables component materials to combine on a substrate in a desired way.

### SUMMARY

The invention features improved methods of forming PZT thin films that  
are compatible with industry-standard chemical vapor deposition production  
techniques. The invention enables PZT thin films having thicknesses of 70 nm or  
25 less to be fabricated with high within-wafer uniformity, high throughput and at a  
relatively low deposition temperature.

In one aspect, the invention features a method of forming a ferroelectric  
PZT film on a substrate. In accordance with this method, a premixed source  
reagent solution comprising a mixture of a lead precursor, a titanium precursor  
30 and a zirconium precursor in a solvent medium is provided. The source reagent  
solution is vaporized to form a precursor vapor. The precursor vapor is  
introduced into a chemical vapor deposition chamber containing the substrate.

Embodiments of the invention may include one or more of the following features.

The zirconium precursor preferably comprises  $\text{Zr}(\text{OiPr})_2(\text{thd})_2$  or  $\text{Zr}(\text{thd})_4$  or  $\text{Zr}(\text{O}^i\text{Bu})_2(\text{thd})_2$ . In one embodiment, the lead precursor is  $\text{Pb}(\text{thd})_2(\text{pmdeta})$ , the  
5 zirconium precursor is  $\text{Zr}(\text{OiPr})_2(\text{thd})_2$ , and the titanium precursor is  $\text{Ti}(\text{OiPr})_2(\text{thd})_2$ . The lead precursor, the titanium precursor and the zirconium precursor preferably have a combined concentration between about 0.05 M and about 1.0 M in solution. The source reagent solution preferably is characterized by lead, zirconium and titanium concentrations between about 5% and 95%.

10 In some embodiments, an oxidizing co-reactant gas comprising 5-100%  $\text{N}_2\text{O}$  and, more preferably 50-75%  $\text{N}_2\text{O}$ , is introduced into the chemical vapor deposition chamber. The oxidizing co-reactant gas also may include  $\text{O}_2$  or  $\text{O}_3$ , or both.

In some embodiments, a second source reagent solution comprising a  
15 second premixed mixture of the lead precursor, the titanium precursor and the zirconium precursor in the solvent medium is provided. The first source reagent mixture preferably is different from the second source reagent mixture. The first and second reagent solutions are mixed to form a precursor solution, and the precursor solution is vaporized to form the precursor vapor. In one embodiment,  
20 the first and second source reagent solutions preferably are characterized by a lead concentration in a range of about 28-65%, a zirconium concentration in a range of about 14-29%, and a titanium concentration in a range of about 20-43%.

The solvent medium preferably comprises an octane-based solvent.

The source reagent solution may be vaporized at a temperature in the  
25 range of about 180-210° C. During deposition, the chemical vapor deposition chamber preferably is maintained at a pressure in a range of about 0.5-10 torr and, more preferably, in a range of about 0.5-4 torr and, still more preferably, at a pressure of approximately 4 torr. The source reagent solution preferably is selected to obtain a precursor vapor having a  $\text{Zr}/(\text{Zr} + \text{Ti})$  ratio in the range of  
30 about 0.05-0.70 and a  $\text{Pb}/(\text{Zr} + \text{Ti})$  ratio in the range of about 0.3-3.0.

The substrate preferably is preheated during a preheating period prior to disposing the substrate on the susceptor. The preheating period may be about 5-30 seconds long. The preheated substrate may be deposited on a heated

susceptor during a heating period prior to formation of the PZT film on the substrate. The heating period may be about 30-60 seconds long or longer. A flow of a purge gas may be provided to reduce film depositions on the susceptor and chamber wall surfaces. In some embodiments, in addition to the purge gas flow, the pre-heating and heating process steps may be performed in a gas flow that includes a combination of one or more of the following gases:  $O_2$ ,  $N_2O$ ,  $O_3$ , and an inert gas (e.g., He,  $N_2$ , or Ar).

Other features and advantages of the invention will become apparent from the following description, including the drawings and the claims.

### DESCRIPTION OF DRAWINGS

FIG. 1 is a diagrammatic representation of a chemical vapor deposition system for forming PZT films.

FIG. 2 is a flow diagram of a method of forming PZT films.

FIG. 3 is a graphical representation of the baseline chemistry for two source reagent precursor mixtures.

FIG. 4A is a diagrammatic representation of a substrate being supported above a heated susceptor during a preheating period prior to the deposition of a PZT film on the substrate.

FIG. 4B is a diagrammatic representation of the substrate of FIG. 4A disposed on the heated susceptor during a heating period prior to the deposition of a PZT film on the substrate.

FIG. 5 is a graph of the  $Pb/(Ti + Zr)$  ratio and the  $Zr/(Zr + Ti)$  ratio in PZT films formed by the method of FIG. 2 plotted as a function of the precursor vapor  $Pb/(Ti + Zr)$  ratio.

FIG. 6 is a graph of z-range plotted as a function of PZT film thickness as measured by atomic force microscopy (AFM) for PZT films deposited in accordance with the baseline chemistry and process conditions described herein.

FIG. 7 is a graph of the  $Pb/(Ti + Zr)$  ratio in PZT films formed by the method of FIG. 2 plotted as a function of the precursor vapor  $Pb/(Ti + Zr)$  ratio for four different CVD chamber pressures.

FIG. 8 is a graph of the  $Pb/(Ti + Zr)$  ratio in PZT films formed by the method of FIG. 2 plotted as a function of the precursor vapor  $Pb/(Ti + Zr)$  ratio

for an oxidizer gas comprising 100% O<sub>2</sub> and an oxidizer gas comprising 50% O<sub>2</sub> and 50% N<sub>2</sub>O.

FIG. 9 is a graph of the Pb/(Ti + Zr) ratio in PZT films formed by the method of FIG. 2 plotted as a function of the precursor vapor Pb/(Ti + Zr) ratio at a CVD chamber pressure of 2 torr and an oxidizer gas comprising 50% O<sub>2</sub> and 50% N<sub>2</sub>O for two different wafer temperatures and constant susceptor temperature of 630° C.

FIG. 10 is a graph of the Pb/(Ti + Zr) ratio in PZT films formed by the method of FIG. 2 plotted as a function of the precursor vapor Pb/(Ti + Zr) ratio at a CVD chamber pressure of 2 torr and an oxidizer gas comprising 25% O<sub>2</sub> and 75% N<sub>2</sub>O for two different wafer temperatures and constant susceptor temperature of 620° C.

### DETAILED DESCRIPTION

In the following description, like reference numbers are used to identify like elements. Furthermore, the drawings are intended to illustrate major features of exemplary embodiments in a diagrammatic manner. The drawings are not intended to depict every feature of actual embodiments nor relative dimensions of the depicted elements, and are not drawn to scale.

Referring to FIG. 1, in one embodiment, a system 10 for forming PZT films by liquid delivery metalorganic chemical vapor deposition includes a chemical vapor deposition (CVD) chamber 12 that is coupled to a dual precursor ampoule liquid delivery system 14 and a single vaporizer 16. CVD chamber 12 may be a 200 mm MOCVD Giga-Cap™ chamber, which is available from Applied Materials, Inc. of Santa Clara, California, U.S.A. CVD chamber 12 includes a gas distribution manifold 18 and a showerhead 20 that is configured to introduce PZT precursor vapor into CVD chamber 12 from which a PZT film may be formed on an exposed surface of a substrate 22, which is supported on a heated susceptor 24. In one embodiment, the spacing between showerhead 20 and susceptor 24 is approximately 7.5-10 mm, and preferably is approximately 8.9 mm. The exposed surface of substrate 22 may correspond to the top surface of a silicon wafer, a layer of silicon dioxide formed on a silicon wafer, gallium arsenide, magnesium oxide, sapphire, or the top surface of a multilayer structure that includes, for

example, a complex integrated circuit that is formed on a semiconductor wafer. In one embodiment, substrate 22 includes a multilayer bottom electrode structure of Ir (100 nm)/TiAlN (100 nm)/Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> that is formed on a silicon wafer. In another embodiment, substrate 22 includes a multilayer bottom electrode structure of IrO<sub>x</sub> (50 nm)/Ir (50 nm)/TiAlN (100 nm)/Si<sub>3</sub>N<sub>4</sub>/SiO<sub>2</sub> that is formed on a silicon wafer.

Liquid delivery system 14 includes a solvent ampoule 26 and a pair of source reagent ampoules 28, 30 containing respective metalorganic mixtures of the component metals needed to form PZT films. Solvent and source reagent ampoules 26-30 are coupled to respective liquid flow controllers 32, 34, 36, which are configured to meter precise quantities of fluid into an equal number of manifolds 38, 40, 42. The metered solvent and metalorganic mixtures are delivered to a final mixing chamber 44 where they are mixed to form a liquid PZT precursor composition. The liquid PZT precursor composition is introduced into vaporizer 16 where the liquid is vaporized, for example, by flash vaporization on a vaporization element (e.g., a porous frit element or a wire grid) that is heated to a suitable temperature to form a precursor vapor. A gas flow controller 46 controls the flow of a carrier gas (e.g., argon gas or helium gas), which transports the precursor vapor into CVD chamber 12 through a valve 47. An additional push gas source (e.g., argon or helium) also may be connected directly to vaporizer 16 through a gas flow controller 45. Gas flow controllers 48, 49, 50 meter precise quantities of oxidizing co-reactant gases (e.g., O<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, or a combination of one or more of these gases) into gas distribution manifold 18, where the oxidizing gases mix with the precursor vapor before being introduced into CVD chamber 12.

Referring to FIGS. 1, 2, 3, 4A, 4B and 5, and initially to FIGS. 1 and 2, a PZT film may be formed on substrate 22 as follows.

During a PZT deposition, a gas flow controller 60 introduces a flow of a purge gas (e.g., argon gas or helium) into CVD chamber 12 to reduce film depositions on the inner wall surfaces of CVD chamber 12 and susceptor 24 (step 63). In one embodiment, the purge gas flow rate is about 250 sccm. During the PZT deposition, the purge gas flow assists in the removal of unconsumed gas molecules, partially reacted compounds and reactive byproducts from CVD



chamber 12 through a valve 51, which is coupled to an evacuation system (or "vacuum foreline") 52. Evacuation system 52 includes several cold traps 54, 56 and 58.

The solvent and metalorganic mixtures contained in ampoules 26-30 are mixed to form a PZT precursor solution (step 64). As mentioned above, source reagent ampoules 28, 30 contain different premixed, concentrated solutions of a lead precursor, a titanium precursor and a zirconium precursor in a solvent medium. In one embodiment, the lead precursor is  $\text{Pb}(\text{thd})_2(\text{pmdeta})$ , the zirconium precursor is  $\text{Zr}(\text{OiPr})_2(\text{thd})_2$ , and the titanium precursor is  $\text{Ti}(\text{OiPr})_2(\text{thd})_2$ . The solvent preferably is an octane-based solvent (e.g., a "G" solvent containing an octane:decane:polyamine mixture in a volume ratio of 5:4:1 and available from Applied Technology Materials, Inc. of Danbury, Connecticut U.S.A). Other embodiments may include mixtures of different Pb, Zr and Ti precursors and solvent systems. In general, the precursors should exhibit good ambient stability, high volatility and good thermal compatibility. For example, in some embodiments, the  $\text{Zr}(\text{OiPr})_2(\text{thd})_2$  zirconium precursor may be replaced by  $\text{Zr}(\text{OiPr})_6(\text{thd})_2$  or  $\text{Zr}(\text{thd})_4$  or  $\text{Zr}(\text{O}^i\text{Bu})_2(\text{thd})_2$ . Each of these precursors is available from Applied Technology Materials, Inc. of Danbury, Connecticut U.S.A.

It has been found that the use of premixed solutions that contain each of the metal precursors enhances the run-to-run repeatability and the throughput of the PZT film forming process relative to processes in which elemental precursors or incomplete precursor mixtures are used. The use of such complete precursor mixtures also enables the use of a single vaporizer, which simplifies the system design. In addition, the use of two such complete precursor mixtures allows the size of the composition space from which precursor solutions may be formed to be reduced substantially, further improving the repeatability of the process while providing sufficient flexibility for process designers to optimize the baseline chemistry to achieve a desired film composition for a given set of process parameters.

As shown in FIG. 3, in some embodiments, the metalorganic precursor composition space includes lead, zirconium and titanium concentrations in the range of 5-95%. In one embodiment, the lead concentration is in the range of about 28%-65%, the zirconium concentration is in the range of about 14%-29%,

and the titanium concentration is in the range of about 20%-43%. The lead precursor, titanium precursor and zirconium precursor have combined concentration of about 0.05-0.5 M in solution and, more preferably, have a combined concentration of about 0.2-0.35 M in solution. In one preferred embodiment, ampoules 28 and 30 each contains  $\text{Pb}(\text{thd})_2(\text{pmdeta})$ ,  $\text{Zr}(\text{OiPr})_2(\text{thd})_2$ , and  $\text{Ti}(\text{OiPr})_2(\text{thd})_2$  with the following respective component metal concentrations:

	Ampoule	Pb Concentration (Molar)	Zr Concentration (Molar)	Ti Concentration (Molar)	Total Concentration (Molar)
Low Pb	28	0.090 (28.6%)	0.090 (28.6%)	0.135 (42.8%)	0.315
High Pb	30	0.205 (64.9%)	0.045 (14.2%)	0.066 (20.9%)	0.316

Table 1

In this embodiment, the reagent solution flow from ampoule 28 is approximately 65-82 mg/minute and the reagent solution flow from ampoule 30 is approximately 118-135 mg/minute for a total reagent solution flow of approximately 200 mg/minute.

After the reagent solutions have been mixed to form the precursor solution, the precursor solution is vaporized to form a precursor vapor (step 66). For the above-described baseline chemistry, the vaporizer temperature preferably is in the range of 180-210° C and, more preferably, is about 190° C. The jackets, lids and other feedthrough apparatus preferably are maintained at the same temperature as vaporizer 16. The carrier gas transports the precursor vapor from vaporizer 16. In one embodiment, the carrier flow through vaporizer 16 is about 250 sccm. Initially, the precursor vapor is diverted to the evacuation system 52 (step 68).

Referring to FIGS. 4A and 4B, while the precursor vapor is being diverted to the evacuation system 52, substrate 22 is loaded onto lift pins 62 inside CVD chamber 12 (step 70). Lift pins 62 are configured to support substrate 22 above heated susceptor 24 during a preheating period in which substrate 22 is heated indirectly by susceptor 24 (e.g., by radiative and convective heating) (step 72).

The preheating process allows substrate 22 to be heated gradually and, thereby, substantially reduces the incidence of thermal shock that otherwise might occur if substrate 22 were placed immediately into contact with susceptor 24. Such thermal shock might cause substrate 22 to break inside CVD chamber 12, in which case CVD chamber 12 would have to be opened and cleaned, a process that substantially reduces the productivity of the system. In one embodiment, the preheating period is about 5-30 seconds long.

After the preheating period has expired (step 74), substrate 22 is lowered into contact with heated susceptor 24 (step 76). In general, substrate 22 may be heated to a final processing temperature of 450-610° C, which is a suitable temperature range for forming a PZT film from the metal constituents of the precursor vapor. In one embodiment, during a heating period, susceptor 24 is set to a temperature of about 640-650° C and heats substrate 22 to a final processing temperature of approximately 600-609°C. In one embodiment, the heating period is about 30-60 seconds long or longer.

After the heating period has expired (step 78), the PZT precursor vapor is mixed with oxidizing co-reactant gases (e.g., O<sub>2</sub>, O<sub>3</sub>, N<sub>2</sub>O, or a combination of one or more of these gases) and the gas/vapor mixture is introduced into CVD chamber 12 to form a PZT film on the exposed surface of substrate 22 (step 80) until a desired PZT film thickness has been deposited (step 81). During the PZT deposition, CVD chamber 12 preferably is maintained at a pressure of about 0.5-10 torr and, more preferably, is maintained at a pressure of about 4 torr. It has been observed that the PZT film deposition rate increases with chamber pressure over the pressure range of 0.5-10 torr. Indeed, the deposition rates in this pressure range are substantially greater than the deposition rates that are achieved at lower chamber pressures (e.g., below 1 torr). Under the above-described preferred deposition conditions, the deposition rate is approximately 12-20 nm/minute and, in one embodiment, the deposition rate is about 16 nm/minute.

In general, the film composition should be tuned so that it falls within the self-correcting Pb composition regime. In addition, within the self-correcting region, the film properties vary significantly with precursor concentration despite the fact that the film remains stoichiometric. Consequently, within the self-

correcting regime, the  $\text{Pb}/(\text{Zr} + \text{Ti})$  (gas) composition should be chosen to optimize film properties. The range of  $\text{Pb}/(\text{Zr} + \text{Ti})$  ratios corresponding to the self-correcting region are dependent on various process conditions, including pressure, substrate temperature, and oxidizer gases.

5 As shown in FIG. 5, for the above-described preferred baseline chemistry and process conditions (which are summarized below in Table 2), a process window yielding single-phase PZT exists that corresponds to a self-correcting Pb composition regime that is characterized by precursor vapor  $\text{Pb}/(\text{Zr} + \text{Ti})$  (gas) ratios between 0.8 and 1.3. Consequently, the starting precursor solutions are  
10 chosen so that this range of compositions is easily accessible. As shown, within this process window, the Zr concentration is substantially independent of the Pb ratio. In general, the resulting PZT films become rougher beyond the self-correcting regime where excess Pb is incorporated into the PZT film. It has been observed that within the self-correcting lead composition regime precursor vapor  
15  $\text{Pb}/(\text{Zr} + \text{Ti})$  (gas) ratios between 1.00 and 1.07 produce PZT films with optimal electrical properties. Accordingly, during deposition, the precursor solution (liquid)  $\text{Pb}/(\text{Zr} + \text{Ti})$  ratio preferably is between 0.3 and 3.0 and, more preferably, is between 0.8 and 1.3 and, still more preferably, is between 1.00 and 1.07. Under these conditions, the precursor solution (liquid)  $\text{Zr}/(\text{Zr} + \text{Ti})$  ratio  
20 preferably is between 0.05 and 0.70 and, more preferably, between 0.30 and 0.40. In one embodiment, the precursor solution (liquid)  $\text{Zr}/(\text{Zr} + \text{Ti})$  ratio is 0.40, which translates to a  $\text{Zr}/(\text{Zr} + \text{Ti})$  ratio of about 0.25 to 0.27 in the resulting PZT film. In the embodiments described above in connection with Table 1, the precursor mixtures in source reagent ampoules 28, 30 have the same  $\text{Zr}/(\text{Zr} + \text{Ti})$   
25 ratio, but have different  $\text{Pb}/(\text{Ti} + \text{Zr})$  ratios, with one source reagent ampoule having a relatively high  $\text{Pb}/(\text{Ti} + \text{Zr})$  ratio and the other source reagent ampoule having a relatively low  $\text{Pb}/(\text{Ti} + \text{Zr})$  ratio.

The baseline process yields 70 nm films with an RMS roughness of 8 nm and a z-range of 58 nm, as measured by atomic force microscopy (AFM). The  
30 dependence of RMS roughness on PZT film thickness is illustrated in FIG. 6.

Heater Temperature	640°C
Wafer Temperature	~ 600°C
Pre-Deposition Time on Chuck	30 sec on-pins / 60 sec on-heater
He Carrier Flow Through Vaporizer	250 sccm
Oxygen Flow	1000 sccm
Ar Purge Flow	250 sccm
Ar Push Gas Pressure on Precursor Ampoules	60 psi
Vaporizer Temperature	190°C
Jackets / Lid / Feedthrough Temperatures	190°C
Showerhead to Heater Spacing	350 mils
Chamber Pressure	4 Torr
Low Pb Precursor Flow	65 to 82 mg/min
High Pb Precursor Flow	118 to 135 mg/min
Total Precursor Flow	200 mg/min
Pb/(Zr + Ti) (in liquid)	1.00 to 1.14
Zr/(Zr + Ti) (in liquid)	0.40
Deposition Rate	~ 160 Å/min
Substrate	Ir (100nm) / Si <sub>3</sub> N <sub>4</sub> / SiO <sub>2</sub> / Si and IrO <sub>x</sub> (50nm) / Ir (50nm) / Si <sub>3</sub> N <sub>4</sub> / SiO <sub>2</sub> / Si

Table 2

5 In addition to proper selection of the precursor solution Pb/(Zr + Ti) ratios, other process parameters have been found to improve the characteristics of the self-correcting Pb composition regime, even at low processing temperatures. For example, it has been discovered that the process pressure and the composition of the oxidizing co-reactant gas have a substantial impact on the  
10 range of the self-correcting Pb composition regime and, consequently, on the degree to which the process temperature may be reduced. In particular, a process pressure of 0.5-4 torr and, more preferably 2 torr, and the addition to the oxidizing co-reactant gas flow of N<sub>2</sub>O in a concentration of 5-100% and, more preferably 50-75% -- with the remaining portion of the co-reactant gas being O<sub>2</sub>,  
15 in this embodiment -- provides a PZT film deposition process with a relatively large self-correcting Pb composition regime, even at a wafer temperature of approximately 575° C.

FIGS. 7, 8, 9 and 10 graphically illustrate the effects of process pressure and N<sub>2</sub>O on the relative size of the self-correcting Pb composition regime. As  
20 shown in FIG. 7, for a constant wafer heater temperature of 630° C, the self-

correcting Pb composition regime extends to lower Pb/(Ti + Zr) (gas) values (and the range of the self-correcting regime increases) as the pressure decreases. As shown in FIG. 8, the self-correcting Pb composition regime extends to higher Pb/(Ti + Zr) (gas) values (and the range of the self-correcting regime increases) when N<sub>2</sub>O is added to the oxidizing co-reactant gas flow. As shown in FIGS. 9 and 10, by combining a low process pressure with an oxidizing co-reactant gas comprising N<sub>2</sub>O, the range of the self-correcting Pb composition regime may be increased significantly, improving the robustness of the deposition process. Two exemplary baseline chemistry and process condition combinations that incorporate these features are summarized below in Tables 3 and 4.

Heater Temperature	630°C
Wafer Temperature	~ 586°C
Pre-Deposition Time on Chuck	30 sec on-pins / 60 sec on-heater
He Carrier Flow Through Vaporizer	250 sccm
Oxygen Flow	500 sccm
N <sub>2</sub> O Flow	500 sccm
Ar Purge Flow	250 sccm
Ar Push Gas Pressure on Precursor Ampoules	60 psi
Vaporizer Temperature	190°C
Jackets / Lid / Feedthrough Temperatures	190°C
Showerhead to Heater Spacing	350 mils
Chamber Pressure	2 Torr
Low Pb Precursor Flow	82 to 115 mg/min
High Pb Precursor Flow	85 to 118 mg/min
Total Precursor Flow	200 mg/min
Pb/(Zr + Ti) (in liquid)	0.79 to 1.00
Zr/(Zr + Ti) (in liquid)	0.40
Deposition Rate	~ 107 Å/min
Substrate	Ir (100nm) / Si <sub>3</sub> N <sub>4</sub> / SiO <sub>2</sub> / Si and IrO <sub>x</sub> (50nm) / Ir (50nm) / Si <sub>3</sub> N <sub>4</sub> / SiO <sub>2</sub> / Si

Table 3

Heater Temperature	620°C
Wafer Temperature	~ 575°C
Pre-Deposition Time on Chuck	30 sec on-pins / 60 sec on-heater
He Carrier Flow Through Vaporizer	250 sccm
Oxygen Flow	250 sccm
N <sub>2</sub> O Flow	750 sccm
Ar Purge Flow	250 sccm
Ar Push Gas Pressure on Precursor Ampoules	60 psi
Vaporizer Temperature	190°C
Jackets / Lid / Feedthrough Temperatures	190°C
Showerhead to Heater Spacing	350 mils
Chamber Pressure	2 Torr
Low Pb Precursor Flow	82 to 115 mg/min
High Pb Precursor Flow	85 to 118 mg/min
Total Precursor Flow	200 mg/min
Pb/(Zr + Ti) (in liquid)	0.79 to 1.00
Zr/(Zr + Ti) (in liquid)	0.40
Deposition Rate	~ 96 Å/min
Substrate	Ir (100nm) / Si <sub>3</sub> N <sub>4</sub> / SiO <sub>2</sub> / Si and IrO <sub>x</sub> (50nm) / Ir (50nm) / Si <sub>3</sub> N <sub>4</sub> / SiO <sub>2</sub> / Si

Table 4

5 After a PZT film having a desired thickness is deposited on substrate 22 (step 81), the PZT precursor vapor again is diverted to evacuation system 52 (step 82). Following deposition, substrate 22 remains within CVD chamber 12 for a post-deposition waiting period before it is transported from CVD chamber 12 into a buffer chamber. In one embodiment, the post-deposition waiting period is  
10 about 5 seconds, or longer.

Other embodiments are within the scope of the claims. For example, in some embodiments, a single source reagent ampoule containing a complete, premixed solution of lead, titanium and zirconium precursors may be used. In other embodiments, three or more complete, premixed source reagent solutions  
15 may be mixed together to define the metalorganic composition space.

Still other embodiments are within the scope of the claims.